

**Mapping Smokeless Powder Residue on PVC Pipe Bomb Fragments Using Total Vaporization Solid Phase Microextraction**

Dana Bors, Ph.D. and John Goodpaster, Ph.D.

Department of Chemistry and Chemical Biology

Forensic and Investigative Sciences Program

Indiana University Purdue University Indianapolis (IUPUI)

Indianapolis, IN 46202

**Corresponding Author:** John Goodpaster

Director of Forensic and Investigative Sciences Program

Indiana University Purdue University Indianapolis

402 North Blackford Street LD326

Indianapolis, IN 46202 United States

317-274-6881

[jvgoodpa@iupui.edu](mailto:jvgoodpa@iupui.edu)

---

This is the author's manuscript of the article published in final edited form as:

Bors, D., & Goodpaster, J. (2017). Mapping Smokeless Powder Residue on PVC Pipe Bomb Fragments Using Total Vaporization Solid Phase Microextraction. *Forensic Science International*.  
<https://doi.org/10.1016/j.forsciint.2017.04.002>

**HIGHLIGHTS**

- Typical concentrations of nitroglycerin on PVC bomb fragments were 15 – 30  $\mu\text{g/g}$
- The highest concentrations of NG were seen on end cap fragments.
- The end caps provide some shielding, which preserves post-blast residues.

The total amount of NG recovered from a PVC device was ~

**ABSTRACT**

Quantitating post-blast explosive residue is not a common practice in crime labs as it is typically not legally relevant. There is value in quantitation, however, if the distribution of residues on Improvised Explosive Devices (IEDs) can help guide future sample collection and/or method development. Total vaporization solid phase microextraction gas chromatography mass spectrometry (TV-SPME/GC/MS) was used to quantify residues of double-base smokeless powder (DBSP), which includes nitroglycerin (NG), diphenylamine (DPA), and ethyl centralite (EC) on post-blast PVC pipe bomb fragments. The analytical method could separate the three constituents in under 5 minutes with a detection limit under 1 ppb, which demonstrates high throughput while maintaining high sensitivity. The method was optimized for nitroglycerin, as it is the most indicative of DBSP. The average mass of nitroglycerin recovered from an entire PVC device was 1.0 mg. The average mass of diphenylamine recovered was much lower (24  $\mu\text{g}$ ) and only one device had detectable levels of EC. The typical concentration of NG on any given fragment was approximately 15 - 30 ppm ( $\mu\text{g NG/g fragment}$ ). However, there was no correlation between the mass of a fragment and the mass of residue upon it. Instead, the residue was distributed such that the highest concentration of residues was found on end cap fragments.

KEYWORDS: Forensic Science, Explosives, Pipe Bomb, SPME

Although it is not commonly known among the public, criminal bombings occur almost daily in the United States. For example, over 36,000 illegal bombing incidents occurred in the United States between 1983 and 2002 leading to over 5,900 injuries and 699 deaths [1]. The most recent statistics from the U.S. Bomb Data Center show that the number of explosive incidents reported in the U.S. has been steadily increasing since 2009. Although the number of people that were injured and killed declined between 2004 and 2007, a large increase is seen in 2013 due to the Boston Marathon Bombing (Figure 1).

Among the various types of Improvised Explosive Devices (IEDs), pipe bombs are easily constructed from readily available materials. Materials such as pipes and endcaps are found in hardware stores, and low explosives are available at sporting goods stores. For example, double base smokeless powder (DBSP) is a deflagrating low explosive that will cause an explosion if contained. In addition to nitrocellulose, DBSP contains the energetic compound nitroglycerin (NG), as well as stabilizers and plasticizers such as diphenylamine (DPA) and ethyl centralite (EC).

Traditionally, analysis of post-blast pipe bomb fragments is limited to qualitative identification of the explosive as the legal issue is what, not how much of an explosive is present [2]. However, there is value to quantitation in explosives research, as it provides information on how devices explode, the amount of explosive residue remaining for analysis, as well as what instrumental sensitivity is required for

analysis. Additionally, mapping of the residue may shed light on which type of fragments tend to have the highest concentration of residues.

Trace analysis of high explosives in complex matrices using absorptive/adsorptive media is an established practice and is routinely applied to explosives investigations. For example, nitroaromatic explosives have been extracted from aqueous samples using a molecularly imprinted silica sorbent and analyzed using liquid chromatography [3]. Direct immersion solid phase microextraction (SPME) coupled with gas chromatography with electron capture detection was utilized to identify and quantitate 2,6-dinitrotoluene, trinitrotoluene, and pentaerythritol tetranitrate from aqueous solutions [4]. Additionally, triacetone triperoxide (TATP) residue from various witness materials was analyzed using headspace SPME with gas chromatography mass spectrometry [5].

There are also many analytical techniques that can be used to detect constituents of smokeless powder, a common filler in pipe bombs. These techniques include liquid chromatography mass spectrometry [6], gas chromatography coupled with thermal energy analysis as well as mass spectrometry [7], and capillary zone electrophoresis [8, 9]. The National Center for Forensic Science's Smokeless Powder Database lists standard operating procedures and instrumental methods for the analysis of smokeless powder. Additionally, the Technical Working Group for Fire and Explosions Analysis (TWGFEX) released a guide in 2009 for the forensic identification of post-blast residues using categorized analytical techniques [10].

Our research group has a long-standing interest in simple IEDs such as pipe bombs. This includes studies of pipe bomb explosions using high speed videography [11, 12], chemical analysis of post-blast residues on pipe bomb fragments [13], and quantitation of explosive residues on witness plates placed immediately adjacent to a pipe bomb [14]. The technique that has been used for all of these studies is Total Vaporization Solid Phase Microextraction Gas Chromatography/Mass Spectrometry (TV-

SPME/GC/MS) [15]. In this method, a solvent extract is completely vaporized inside a headspace vial and the vapor is then sampled using SPME. As TV-SPME completely vaporizes the liquid extract, an equilibrium is established between the vapor phase analyte and the SPME fiber coating. In comparison to liquid injection of organic extracts, TV-SPME increases the sensitivity by an order of magnitude, allowing lower concentrations and larger sample volumes to be analyzed.

Prior work on fragments from steel pipe bombs determined that the total mass of NG recovered from the remains of an eight inch steel device ranged from 0.47 – 2.2 mg, with concentrations on individual fragments ranging from 1.1 – 3.0 ppm ( $\mu\text{g/g}$ ) [13]. In contrast, the concentration of DPA and EC were 1 – 2 orders of magnitude lower [13]. The distribution of residues in steel devices was clearly not homogenous in that fragments from the end caps of the devices had residue concentrations that were 10 – 100 times higher than fragments from the pipe body.

In a similar study, DBSP residues were quantitated on witness plates suspended immediately adjacent to PVC pipe bombs [14]. The concentration of NG was extremely varied, with essentially no NG detected on the witness plate that was facing the fused end of the device. In contrast, the four witness plates that faced the pipe body (top, bottom, right and left) all collected substantial amounts of residue. The pipe body corresponds to the location where PVC devices first begin to fail [11, 12].

This paper focusses on PVC pipe bomb fragments, which have yet to be studied. As was done previously, the amount and distribution of explosive residues on PVC pipe bombs was determined by TV-SPME/GC/MS. PVC devices are known to fail much more slowly and fragment more extensively than steel devices. In addition, and unlike steel devices, PVC devices first fail along the pipe body as both the end caps are cemented to the pipe body which has similar strength. Therefore, our working hypothesis was that the amount and distribution of explosive residues on PVC would necessarily differ from steel.

## Materials and Methods

### *Materials*

PVC pipe (8" x 1" diameter) and PVC endcaps (1" diameter) were purchased at Home Depot, and Alliant Red Dot double base smokeless powder was obtained from Gander Mountain in Indianapolis, IN. SPME vials and PTFE caps were acquired from Gerstel. Polyethylene glycol SPME fibers, ethyl centralite (99%), and acetone were obtained from Sigma Aldrich. Standards of nitroglycerin (1 mg/mL) and diphenylamine (ACS grade) were purchased from Restek and Acros Organics respectively.

### *Pipe Bomb Construction and Initiation*

The constructed pipe with endcaps were divided into three sections:

- 1) Left endcap (1.8 in length x 1.2 in diameter) and one third of the pipe body (1.2 in diameter x 2.67 in length). When assembled, these sections had an internal surface area of approximately 11.2 in<sup>2</sup>.
- 2) Middle section of the pipe body (1.2 in diameter x 2.67 in length). These sections had an internal surface area of approximately 10 in<sup>2</sup>.
- 3) Right endcap (1.8 in length x 1.2 in diameter) and one third of the pipe body (1.2 in diameter x 2.67 in length). When assembled, these sections had an internal surface area of approximately 11.2 in<sup>2</sup>.

Each section was color coded with white, black, or orange paint. Only three color zones were used in this study due to the high fragmentation that was anticipated, the tendency of PVC end caps to remain adhered to the pipe body post-blast and the difficulty of differentiating end cap fragments from pipe body fragments. Determining the distribution of residues in a higher "resolution" experiment (e.g., more than three distinct zones) remains a goal for future studies.

Cages constructed of a welded steel frame and two layers of metal grating were used to contain the PVC fragments while simultaneously venting blast pressure. The setup is shown in Figure 2. Approximately 50 g of DBSP was used in each device. A time fuse was used as the initiation mechanism (inserted into the white endcap). The three devices were assembled, suspended, and initiated by the Indiana State Police Bomb Squad. After the explosions, fragments from within the cages were collected by gloved personnel and placed in paint cans specific to each device.

#### *Cataloging Fragments*

The fragments were first photographed as an ensemble. Then, the pipe bomb fragments were sorted by pipe location/color. Each fragment was assigned an identification number per the convention, “device number – location – fragment number”. Fragments were photographed individually, weighed, and placed in plastic bags. Given the extent of fragmentation seen in PVC when using DBSP as a filler, the smallest fragments were pooled into 10 mg batches and extracted as a group.

#### *Preparation of Standards and Extraction of Fragments*

For this study, calibrants for nitroglycerin, diphenylamine, and ethyl centralite were prepared in acetone at concentrations ranging from 25 ppb – 1 ppm. Pipe bomb fragments were placed in one of three extraction jars based on fragment size. An amount of solvent (acetone) was added (i.e., 50 mL, 20 mL, or 10 mL) so that all fragments were covered. The jars were sealed and placed on a shaker table for 15 min. Then, 55  $\mu$ L of the acetone extract was transferred to a SPME vial for analysis. Note that dichloromethane, although a popular and effective extraction solvent for post-blast debris, swells and dissolves PVC and cannot not be used under these circumstances.

#### *Chemical Analysis*

Samples were incubated at 60 °C for 5 min. A polyethylene glycol fiber was then inserted and exposed inside the SPME vial for 20 min. These parameters were optimized as described previously. After sample extraction, the SPME fiber was inserted into the inlet of the GC and desorbed for 1 min. The GC inlet was operated in PTV mode with an initial temperature of 200 °C held for 0.21 min, ramped 10 °C/s to 250 °C and held for 0.21 min with a splitless time of 1 min to correspond to the SPME desorption time. After desorption, the SPME fiber was then conditioned for 3 min at 240 °C. Analytes were separated on a ZB-5MS column (10 m x 0.18 mm x 0.18 µm) using helium as the carrier gas at a flow of 1.5 mL/min. The oven program began at 40 °C for 1 min, ramped at 45 °C/min to 220 °C, ramped infinitely to 300 °C, and held for 1 min. The transfer line to the MS was held at 250 °C. Pulsed positive ion negative ion chemical ionization (PPINICI) was used as the ionization technique. Methane was the carrier gas used for chemical ionization (1.3 mL/min). Selected ion monitoring (SIM) was used for analyte detection, with positive ions of  $m/z$  170 and 269 and a negative ion of  $m/z$  62.

## Results and Discussion

### *Macroscopic Examination*

Fragments were first sorted by their color, corresponding to their initial pipe location (Figure 3). The number of recovered fragments differed from device to device, but the overall range was 757–864 fragments for the three PVC devices. Each piece was examined macroscopically for intact smokeless powder particles, which were not found on any fragment. No fracture matches were apparent with the PVC fragments. Individual fragment masses were summed for the aggregate total. The average recovery by mass was 56%. Many of the pipe body fragments exhibited multiple colors, so PVC fragments containing two colors were sorted into the color category that was most prevalent.

### *Quantitative Mapping of Smokeless Powder Constituents*



The performance of this analytical method has been fully investigated and it is summarized elsewhere [13], but a few key points are highlighted here. Using a PEG fiber, the linear range for nitroglycerin spanned three orders of magnitude (from 5 ppb to 5 ppm) with a linearity of 0.997. In addition, when compared to liquid (splitless) injection, TV-SPME is approximately ten-fold more sensitive and TV-SPME generates signal-to-noise ratios that are approximately ten-fold higher. Based upon the relationship between signal-to-noise and NG concentration, we estimated a detection limit of approximately 100 ppt [13].

The mass of residue recovered by location are shown in Table 1, and distributions of these values are depicted as heat maps in Figure 4. In all cases, the greatest amount of residue was located on the endcaps, even if the results are corrected for the slightly larger internal surface area of the end cap segments. Furthermore, the fused endcap yielded more residue than the non-fused endcap in all three devices. Similarly, the most concentrated areas of DPA were also the endcaps (Figure 5). Accumulation of post-blast residues on the end caps of PVC devices was unexpected given that steel devices, which first fail at the end caps, also accumulate the greatest residue at those locations. In contrast, PVC devices fail first along the pipe body. This may indicate that the mechanism by which pipe bombs fail in the first moments of an explosion is not as important as the physical shielding offered by the end caps.

The average quantity of NG recovered from each device was approximately one milligram (the same as was seen with steel devices). The average quantity of DPA recovered from each device was much lower than NG, only averaging 24  $\mu\text{g}$ . Finally, only one device had a level of EC that were above the LOD resulting in a total mass of 0.8  $\mu\text{g}$ . These results are not surprising given that the method was optimized for recovery of NG. A much higher extraction temperature would be needed to more efficiently vaporize and extract DPA and EC.

A histogram was generated to depict the mass of NG recovered per fragment (Figure 6). The mass of NG recovered per fragment fell over a relatively narrow range (i.e., between 0 and 216  $\mu\text{g}$ ). The most common amount of NG found on a fragment was between 25 and 50  $\mu\text{g}$  of NG. The most-straightforward protocols for post-blast analysis involve a solvent extraction of one or more fragments using a solvent such as acetone (for PVC) or dichloromethane (for steel). Based upon this result, one could conceive of using a milliliter of solvent, resulting in an extract concentration of 25 – 50  $\mu\text{g}/\text{mL}$ . To most analysts conducting GC/MS, this is a low but by no means undetectable concentration.

When a histogram is made of the concentrations of the analytes (in  $\mu\text{g}$  residue/g fragment), the concentration of NG fell between 0 and 114  $\mu\text{g}$  NG/g fragment. The most common concentration of NG was between 15 - 30  $\mu\text{g}/\text{g}$ . It is important to note that these concentrations are approximately 100 times higher than those seen in steel devices. However, this does not mean there is a large difference in the efficiency with which steel devices deflagrate. It is the higher density (and hence higher mass) of steel fragments that results in low concentrations. This is further supported by recalling that the total amount of NG recovered from an entire device was quite similar for both PVC and steel devices.

It was also determined that there is no correlation between the mass of the fragments and the mass of NG recovered from the fragments. This is not surprising as the distribution of NG on the fragments is not uniform and, therefore, does not scale with fragment mass. Perhaps a better metric would be calculating the mass of NG per unit area of a fragment. The difficulty with this approach when working with PVC fragments is that the fragments are small and highly irregular, making a surface area measurement difficult or even impossible. A surface area approach could be quite useful when examining witness plates, however.

Overall, the amount of explosive residue left on the remains of a PVC device is small but not inconsequential (i.e., 1.0 - 1.2 mg for NG and 21 - 28  $\mu\text{g}$  for DPA). The typical amount of NG found on a

PVC fragment ranged from 25 – 50  $\mu\text{g}$ , and typical concentrations ranged from 15 – 30 ppm (w/w). It follows that the detection limit of any analytical technique that is proposed or intended for post-blast analysis should be below this level. This requirement is not trivial but it is also not onerous given the high sensitivity of modern instrumentation. Lastly, and as was seen in steel devices, explosive residues were not uniformly distributed – they are instead found at much higher levels on fragments from the end caps of the devices. Although high speed video depicts PVC pipe bombs as failing first along the pipe body itself, it appears that the ability of one end cap to partially contain the initial flame front and the ability of the second end cap to resist the propagation of the flame front is of greater importance. Taken together with our past results, we can state that while the explosion from a PVC pipe bomb is projected outward from the pipe body (i.e., the “sides” of the device), the end caps provide partial shielding from the high temperatures of the deflagration. This allows for post-blast residues to persist in these shielded locations and, therefore, generate the most valuable fragments for chemical analysis.

#### *Acknowledgements*

The authors would like to thank members of the Indiana State Police Bomb Squad, specifically Officer Benjamin Cook for their assistance in assembling and initiating the PVC devices. The authors acknowledge Tony Bors for assembling the containment structures. Finally, the authors acknowledge all of the IUPUI students who assisted at the event

## References:

- [1] Kapur GB, Hutson HR, Davis MA, Rice PL. The United States twenty-year experience with bombing incidents: implications for terrorism preparedness and medical response. *Journal of Trauma and Acute Care Surgery*. 2005;59:1436-44.
- [2] Beveridge A. *Forensic Investigation of Explosions*. International Forensic Science and investigation Series. 2nd ed: CRC Press; 2011. p. 792.
- [3] Lordel-Madeleine S, Eudes V, Pichon V. Identification of the nitroaromatic explosives in post-blast samples by online solid phase extraction using molecularly imprinted silica sorbent coupled with reversed-phase chromatography. *Anal Bioanal Chem*. 2013;405:5237-47.
- [4] Ahmad UK, Kiu KH. Solid Phase Microextraction–Gas Chromatography For The Analysis Of Explosives In Post Blast Water Samples. *Jurnal Teknologi*. 2012;46:59–74.
- [5] Stambouli A, El Bouri A, Bouayoun T, Bellimam MA. Headspace-GC/MS detection of TATP traces in post-explosion debris. *Forensic Science International*. 2004;146, Supplement:S191-S4.
- [6] Mathis JA, McCord BR. Mobile phase influence on electrospray ionization for the analysis of smokeless powders by gradient reversed phase high-performance liquid chromatography-ESIMS. *Forensic Science International*. 2005;154:159-66.
- [7] Muller D, Levy A, Vinokurov A, Ravreby M, Shelef R, Wolf E, et al. A Novel Method for the Analysis of Discharged Smokeless Powder Residues. *Journal of forensic sciences*. 2007;52:75-8.
- [8] Hopper KG, McCord BR. A comparison of smokeless powders and mixtures by capillary zone electrophoresis. *Journal of forensic sciences*. 2005;50:307-15.
- [9] Smith KD, McCord BR, MacCrehan WA, Mount K, Rowe WF. Detection of Smokeless Powder Residue on Pipe Bombs by Micellar Electrokinetic Capillary. *Electrophoresis*. *Journal of forensic sciences*. 1999;44:789-94.
- [10] TWGFEX. Recommended Guidelines for Forensic Identification of Post-Blast Explosive Residues. 2009.
- [11] Bors D, Cummins J, Goodpaster J. The anatomy of a pipe bomb explosion: measuring the mass and velocity distributions of container fragments. *J Forensic Sci*. 2014;59:42-51.
- [12] Bors D, Cummins J, Goodpaster J. The anatomy of a pipe bomb explosion: The effect of explosive filler, container material and ambient temperature on device fragmentation. *Forensic Sci Int*. 2014;234:95-102.
- [13] Bors D, Goodpaster JV. Mapping explosive residues on galvanized pipe bomb fragments using total vaporization solid phase microextraction (TV-SPME). *Analytical Methods*. 2015.
- [14] Sauzier G, Bors D, Ash J, Goodpaster JV, Lewis SW. Optimisation of recovery protocols for double-base smokeless powder residues analysed by total vaporisation (TV) SPME/GC-MS. *Talanta*. 2016;158:368-74.
- [15] Rainey CL, Bors DE, Goodpaster JV. Design and Optimization of a Total Vaporization Technique Coupled to Solid-Phase Microextraction. *Analytical Chemistry*. 2014;86:11319-25.

Figure 1

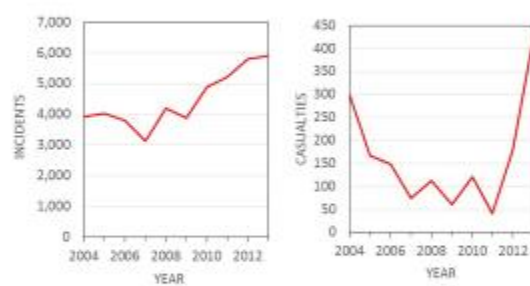


Figure 2



Figure 3



Figure 4

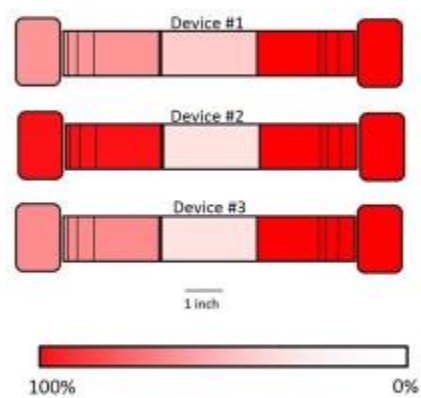




Figure 5

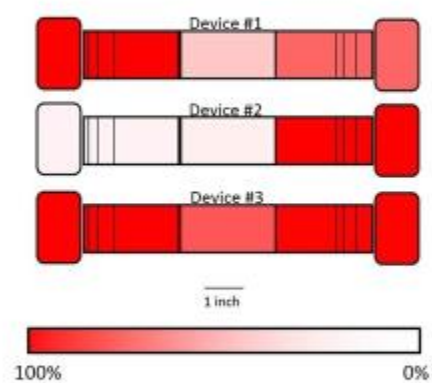


Figure 6

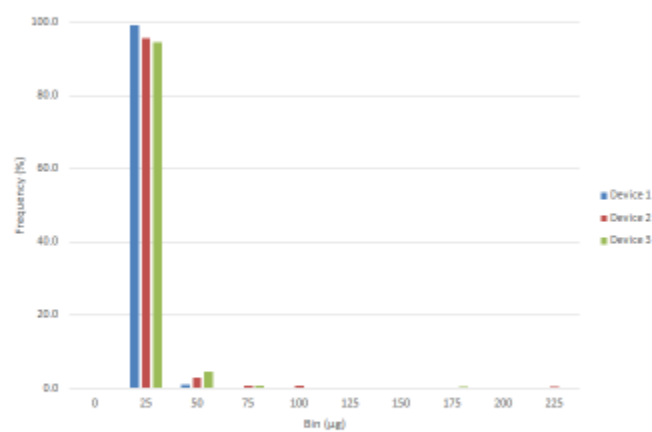


Figure 7

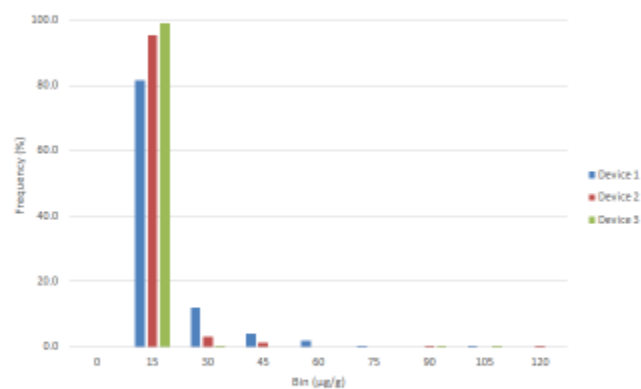


Table 1

Device	Endcap 1 Mass ( $\mu\text{g}$ )	Pipe Body 1 Mass ( $\mu\text{g}$ )	Pipe Body 2 Mass ( $\mu\text{g}$ )	Pipe Body 3 Mass ( $\mu\text{g}$ )	Endcap 2 Mass ( $\mu\text{g}$ )	Total Mass (mg)
PVC 1	245.0	118.2	602.9			0.9661
PVC 2	559.1	65.8	600.2			1.2251
PVC 3	297.0	70.1	659.5			1.0266